

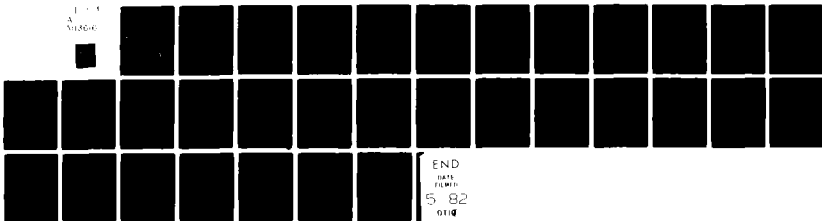
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A Summary and an Index of Work Completed  
Under the Task NR. 051-162 and NR. 384-305

by

M.A. Barrett-Gültepe, M.E. Gültepe  
and E. Yeager

February 25, 1982

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## I. Introduction

This is the summary report for work done under the general title "Ultrasonic Waves and Electrochemistry" task numbers 051-162 and 384-305. During the years October 1, 1948 to December 31, 1981. Starting January 1953, the task number was changed to 384-305 and continued until December 31, 1981.

The work done under the title "Ultrasonic Waves and Electrochemistry" can be divided into five main groups:

1. The use of ultrasonic waves as a tool in the study of electrolytic solutions, hydrated ionic melts and electrochemical interfaces.
2. Ultrasonic study of colloidal dispersions and sediments in electrolytic solutions.
3. Promotion of chemical and electrochemical effects by ultrasonic waves.

In Appendix A the list of publications produced under the contract research is given and references cited in the following text refer to this list. In Appendix B the list of technical reports prepared under the task numbers NR. 051-162 and NR. 384-305 is given. Finally, in Appendix C, a list of the accomplishments of the work sponsored by these two task numbers and the significance of these results to the Navy and Physical Acoustics are given.

## II. The use of ultrasonic waves as a tool in the study of electrolytic solutions, hydrated ionic melts and electrochemical interfaces

When acoustical waves are propagated through an electrolyte solution, small a.c. potentials are generated between points separated by a phase distance other than a multiple of one half the wavelength. These a.c. potentials were predicted on theoretical grounds by Peter Debye in 1933 but not experimentally found until 1948 in work at this university<sup>2,4</sup> (Technical Report No. 2).

The effect occurs principally because of differences in the dynamic reaction of the cations and anions to the sound field (inertial and pressure gradient effects). Subsequent theoretical work as part of the ONR research has shown that the effect provides a measure of the partial molal volumes of the individual ions and hence ion solvent interactions.

This effect (originally called the Debye effect but more recently ionic vibration potential) was originally detected using inert electrodes in the electrolyte and a standing wave technique to differentiate between the true effect and cross talk (electromagnetic coupling). In the 1960's much further work was done on the effect using pulse modulated ultrasonic waves and the much slower propagation time of the sound waves compared to the speed of light to differentiate between the true effect and crosstalk. The pulse technique facilitated quite quantitative measurements of the small potentials [ $\sim 1 \mu\text{V}$  per unit velocity amplitude (1 cm/s)] and yielded the most reliable value for the individual partial molal volumes now available [see Technical Report No. 45]. The measurement of the effect has been carried out not only in a large number of electrolytes but also in polyelectrolytes and micelle systems. Its usefulness has proved far greater than ever envisioned by Debye.

The first systematic and quantitative studies of ionic vibration potential were performed only in 1966. The use of a double probe assembly partially immersed in the solution under investigation<sup>32,36</sup> provided the experimental verification of several predictions of the most thorough theoretical treatment of the ionic vibration potential, given in 1947.<sup>1</sup> On the other hand, a closer examination of the physical meaning of the apparent molar masses of the solvated ions which appear in this treatment indicated that the ionic vibration potential is closely related to a weighted difference between the partial molal volumes of the ions present in the system.<sup>32,36</sup>

It thus became possible by combining the value of the ionic vibration potential for a given electrolyte in a given solvent, and the partial molal volume at infinite dilution for the same electrolyte in the same solvent to obtain the values of the partial molal volumes of the individual ions constituting this electrolyte. This was done between 1966 and 1968 for a series of electrolytes of widely differing nature in aqueous solutions.<sup>36,39,40,42</sup>

In addition to ionic vibration potential, the first detection and preliminary measurements of polyelectrolyte vibration potential were made in this laboratory in 1962.<sup>26</sup> With the development of the sophisticated apparatus made for ionic vibration potential measurements, quantitative measurements of polyelectrolyte vibration potential with accuracies of  $\pm 5\%$  are reported in Technical Report No. 30 from this study. The following conclusions were reached:

1. Polyelectrolyte vibration potentials depend on the nature, concentration, and percent neutralization of the polyelectrolyte as well as on the nature of the gegenion and on the nature and concentration of any added salt.
2. The experimental results are in quantitative agreement with theory based on the ionic vibration potential mechanism and the polymer bead model.
3. The polyelectrolyte vibration potential can be used to determine the partial molal volume of a monomer unit in the polymer bead model. (The value is  $45.6 \text{ cm}^3/\text{mole}$  for unneutralized polyacrylic acid.)

In Technical Report No. 31, the results were given for the ultrasonic vibration potential measurements in tetra alkylammonium halides at 220 kHz. The experimental and theoretically predicted values were in good agreement at low concentrations.<sup>39</sup> The concentration dependence can be explained in

terms of cation-cation pairs and ion triplets provided the volumes of these aggregates are much less than the sum of the volumes of the separate ions. A.C. potential components can also be generated at electrode-solution interfaces, particularly in dilute electrolytes.

An interesting electrokinetic effect<sup>12</sup> has been studied for the first time in our laboratory with pulse modulated ultrasonic waves (see Technical Report No. 5). If a wire with a fiber covering is placed in a dilute solution of an electrolyte and exposed to ultrasonic waves, a.c. potential differences are developed between the wire and the bulk of the surrounding solution. The dependence of this effect on solution parameters as well as the type of porous covering clearly indicates that the effect is associated with the diffuse layer of ions surrounding the fibers, and hence, is electrokinetic in nature. Quantitative measurements have been made at 200 kHz and the electro-acoustic response of the cotton covered copper wire in  $1 \times 10^{-4} \text{M NaCl}$  solution is  $5 \times 10^{-8}$  volts per dyne  $\text{cm}^{-2}$ . The frequency dependence of this effect was also studied and it was found that at 1 MHz, there was a decrease of approximately 10 dB in the electro-acoustic response. Besides its possible use as a velocity sensitive acoustical probe, it can be used to study electrokinetic effects involving fibers and porous coatings.

In addition to these electrokinetic effect studies, a.c. and d.c. streaming potential measurements were made with porous packings consisting of ion exchange resins, pyrex glass wool, nylon and surgical cotton in a large number of aqueous solutions. In contrast to d.c. streaming potential measurements, when the velocity of the liquid flow through the porous packing is sinusoidal, a.c. streaming potentials are produced between the opposite sides of the packing. Special apparatus was developed for the a.c. streaming potential measurements at frequencies up to 30 Hz. No frequency dependence was found over the limited frequency range involved in the present work. The dependence of



the streaming potential on type and concentration of electrolyte solution is the same as would be predicted on the basis of established theories for conventional d.c. methods. The experimental results obtained by a.c. and d.c. streaming potential measurements are in complete agreement (see Technical Report No. 21).

If sound waves impinge on an electrode at which a gas is being liberated by electrolysis an alternating potential is produced on the electrode relative to the bulk of the surrounding solution. The amplitude of the so-called "alternating components in electrode potential" is dependent on the acoustical amplitude, the polarizing current density and the conductance of the solution, but is essentially independent of the base metal upon which the hydrogen gas is evolved. The acousto-electrochemical effect has been explained at ultrasonic frequencies in terms of the modulation of the  $i$ - $r$  drop in the solution in the immediate vicinity of the electrode through periodic variations in the size of the gas bubbles found at the electrode surface.<sup>4,5</sup> (See Technical Reports Nos. 3, 8, 9) It has been suggested that the "alternating components in the electrode potential" effect might be used in the form of an extremely small probe for the determination of phase and amplitude at ultrasonic frequencies, particularly above 100 kHz.

As we mentioned before, when ultrasonic wave impinge on an electrode immersed in electrolyte, various a.c. effects are produced. The converse of such effects is produced when an a.c. potential is applied to an electrochemical interface relative to the bulk electrolyte. Periodic volume changes are produced at the solution side of a metal-electrolyte interface. This in turn gives rise to the generation of sound waves of the same frequency in the solution phase. The Technical Report No. 44 describes the first detection of these sound waves using a gold electrode in an acid electrolyte. Preliminary measurements were reported as a function of d.c.

(bias) electrode potential.<sup>55,56</sup> It was also found that the effect was particularly sensitive to adsorbed species such as organics. This is not surprising since such species adsorb strongly on the electrode at various potentials and can also undergo faradiac processes yielding various oxidation and reduction products. This effect was found to be too small to be a practical source for sound generation. It is possible, however, to enhance the effect by stacking a number of very thin electrodes with very small electrolyte gaps. The main use of this effect, however, is the study of adsorbed species and anodic film formation on metal surfaces in electrolytes.

Ultrasonic absorption measurements provide a means for studying the kinetic parameters of processes which occur too rapidly to be studied by conventional techniques.<sup>29</sup> Specific processes such as unimolecular and dissociation reactions, proton-transfer reactions (e.g. hydrolysis or acid-base dissociation) can be studied by ultrasonic absorption and several other relaxation techniques. Investigations of relaxation times shorter than  $10^{-6}$  s, are suitable for ultrasonic absorption measurements. During the contract research various apparatus were built to cover the range 0.03 to 550 MHz. A survey of some of the salient features of these are given in Table I. Details are given in Technical Report Nos. 32 and 35. The spherical resonator apparatus has more recently been updated to incorporate computer control allowing much more detailed measurements without undue expenditure of the experimenters time (see Technical Report No. 48).

A review of ultrasonic relaxation in electrolytic solutions is given in Technical Report No. 25. Ultrasonic relaxation was re-examined in  $\text{MgSO}_4$  solutions in order to resolve discrepancies in published data.<sup>31,43</sup> Two relaxation frequencies were found adequate to describe the data if the non-relaxation absorption is treated as an adjustable parameter, in contrast to the 3 or 4 relaxation frequencies reported earlier by other groups (Technical

Report Nos. 35 and 37). Further work done on some other 2:2 electrolytes (copper sulfate and cobalt sulfate) indicated that the high frequency absorption peak could be attributed to the diffusion controlled second order process leading to the formation of an encounter complex (see Technical Report No. 32).

In Technical Report No. 26 a study of the kinetics of the hydrolysis of the cyanide ion is described, using ultrasonic absorption measurements<sup>28</sup> over the frequency range 30 kHz to 25 MHz. A single relaxation frequency was observed which depends on concentration in a manner expected theoretically for the hydrolysis reaction. Similarly, a single relaxation was found<sup>44</sup> in acetic acid, agreeing with the calculations on the equilibrium and kinetic parameters for the ionization of acetic acid determined by other techniques. The data yielded values for  $k_{\text{dissoc}}$ ,  $k_{\text{assoc}}$  and  $\Delta V$ . The measurements of relaxation times for chemical processes slower than  $10^{-5}$  s cannot be determined with accuracy by ultrasonic measurements. The lowest frequency obtainable by the 100-liter titanium spherical resonator in use in our laboratory is 20 kHz.

Apparatus for pressure step and shock wave measurements were first developed<sup>41</sup> as part of the ONR research (Technical Report No. 27) and used to measure the relaxation times extending from  $10^{-7}$  to the half life of a graduate student in this university for various chemical processes involving ionic equilibria. The pressure step method involves the sudden release of an applied static pressure on an electrolytic solution. After the pressure release the re-establishment of equilibrium between free hydrated ions and associated species is followed by means of conductance measurements. Relaxation times longer than 50  $\mu$ s can be measured with this apparatus. This method was applied to the study of complex formation between polyvalent cations and various ligands (Technical Report No. 35).

Many of the more interesting association-dissociation processes involving transition metal complexes have relaxation times shorter than 50  $\mu$ s and hence cannot be studied with the above techniques. A much faster pressure rise can be accomplished by utilizing the non-linear properties of the transmitting liquid to sharpen up a shock front. The velocity of sound in a liquid increases with pressure and consequently the leading edge of a pressure pulse will steepen as the pulse is propagated through the liquid. In contrast, a dilatation pulse, such as is produced in the pressure step technique, will flatten out. The pressure-shock technique was demonstrated to be a relatively simple means for measurement of relaxation times for chemical processes in the range  $10^{-6}$  to  $10^{-3}$ . Details are given in Technical Report No. 33.

The low frequency relaxation in sea water, indicated by a long range sound propagation, was investigated using temperature-jump measurements<sup>48</sup> in which a hydrogen ion sensitive color indicator was added to permit optical readout. The measurements indicated a single relaxation at  $1.5 \times 10^{-4}$  s at 9.7°C originating from boron with the  $B(OH)_3 - B(OH)_4$  as the likely relaxation process. This was the first time that equilibrium involving borate-boric acid exhibited a relaxation frequency at  $\sim 1$  kHz and was responsible for the corresponding relaxation sea waters.

Acoustic measurements are difficult above 550 MHz. In order to gain insight into relaxation phenomena above this range, it is necessary to employ optical techniques. Brillouin scattering studies on a number of electrolytes,<sup>50,52</sup> including halides, nitrates and sulfates, yielded hypersonic velocity data from the frequency shift of the Brillouin components, and hypersonic absorption coefficients from the line widths. The results compare favorably with those from ultrasonic velocity and absorption data at lower frequencies. The ratio of the light intensity of the Rayleigh component to that of the Brillouin line

was compared with theory, and agreement was found for solutions of alkali halides and alkali earth halides and nitrates, confirming simple concentration fluctuation theory. However, solutions of 2:2 sulfates gave intensity ratios significantly higher than theory. Brillouin scattering and ultrasonic measurements were both utilized to investigate the high frequency (5 MHz to 12 GHz) relaxations of zinc nitrate and calcium nitrate hydrate melts. A distribution of relaxation times was observed. These high frequency studies are given in Technical Report No. 40, 41 and 43.

### III. Ultrasonic study of colloidal dispersions and sediments in electrolytic solutions

When sound waves are propagated through a colloidal suspension in an electrolyte, much larger a.c. potentials are generated than just in an electrolyte. This effect also occurs because of differences between the displacement of the colloidal particle and the ions of the system. Each charged colloidal particle is surrounded by an ionic atmosphere or diffuse ionic cloud which is normally symmetrical. In the presence of the sound waves this ionic atmosphere is periodically distorted, giving rise to periodic oscillating dipoles. This in turn results in "colloidal vibration potential". This much larger effect was first detected by A.J. Rutgers in 1938. Quantitative studies of the effect have also been carried out as part of the ONR research. The effect is a powerful tool for checking the theoretical models for charge distribution about colloidal particles. This is intrinsic to the electrolyte and colloid-electrolyte media through which the sound waves are propagated.

Measurements on colloidal vibration potential were made in colloidal silica suspensions at frequencies from 200 kHz to 1.2 MHz as a function of

particle size, colloidal concentration and ionic strength. In this work, corrections have been made for the electrical loading effects of the measuring equipment for suspensions of very low conductances. Quantitative colloidal vibration potentials in silica suspensions were measured in 1960 and the results were presented in Technical Report No. 23. The experimental values for the colloidal vibration potential are in reasonably good agreement with values calculated from the treatment of this effect by Enderby, particularly for suspensions of relatively high specific conductance.

Ultrasonic vibration potential measurements were also made in solutions of salts exhibiting micelle formation. Experimental data indicated that in dilute solutions of sodium lauryl sulfate at concentrations far below the critical micelle concentration, the vibration potentials agree well with the theoretical values. The concentration dependence of the vibration potential in various micelle solutions show that at concentrations below the critical micelle concentration there is strong evidence for the formation of charged aggregates which were representing the nuclei for micelles. Ultrasonic vibration potential can be used to determine the critical micelle concentration.

The propagation of sound in concentrated colloidal dispersions and marine sediments was theoretically and experimentally studied with particular attention to the influence of interfacial phenomena. The following model colloid systems were chosen: kaoline, montmorillonite, polystyrene latex particles and PVA (polyvinylacetate-polyvinylalcohol block co-polymer). For the first time, the effect of hetero-deflocculation of two dissimilar mineral grains on the velocity of sound was established in concentrated dispersions in the case of kaoline and montmorillonite mixtures (see Technical Report No. 46).

It had been shown in earlier work on polystyrene latex dispersions by M.A. Barrett Gultepe, D.H. Everett and M.E. Gultepe that acoustic absorption in the dispersions is strongly influenced by the nature of the electrolyte-particle interface, and that an adsorbed layer of PVA considerably alters the acoustic absorption properties. Sound velocity measurements made in this laboratory on a similar system as a function of temperature yielded compressibility values for the PVA covered latex that differed from that expected from the simple additivity effect of the two components. At low temperatures the low compressibility found may be due to the hydrophobic interaction between acetate groups and the polymer backbone (Technical Report in preparation).

Ultrasonic waves have also proved useful in producing emulsion.<sup>34</sup> This phenomena was studied in our laboratory using electron microscopy to examine the particle size distribution with freeze type techniques. A surprising result is that the particle distribution has certain narrow ranges of size completely missing. These size droplets are apparently unstable in the sound field and depend on the frequency. Attempts to predict such instabilities on the basis of surface wave models, however, were not fully successful. Furthermore, some of the missing sizes corresponded to subharmonics.<sup>34</sup>

#### IV. Promotion of chemical and electrochemical effects by ultrasonic waves

Electrodeposition of copper experiments in the presence of ultrasonic waves at 200 kHz and 1 MHz at  $1 \text{ watt cm}^{-2}$  were made in our laboratory (see Technical Report No. 10). The schlierer technique was used to examine the concentration gradients at the cathode and anode during the electrodeposition of copper. The ultrasonic waves seem to remove completely these concentration

gradients at reasonable current densities. The deposition of copper, as involved in the above study, however, is characterized by low activation polarization and negligible simultaneous hydrogen evolution. In Technical Report No. 15 the effects of ultrasonic waves on the structure of the electrodeposited nickel during the hydrogen evolution were reported. X-ray diffraction studies of the deposits indicate that the ultrasonic waves decrease the tendency for the 110 planes of the face centered cubic system to be oriented parallel to the electrode surface at high current densities and increase the tendency for the 100 planes to be oriented parallel to the surface at low current densities.

All the contract research done on the subject of the effects of ultrasonic waves on the electrodeposition of metals lead to the conclusion that the ultrasonic effects are generally an extension of what is encountered with increased agitation of a more conventional nature. Ultrasonically produced cavitation is therefore one of the most effective ways of promoting mass transport to and from solid-liquid interfaces.

When high intensity sound waves propagate through liquids, chemical reactions often occur within the liquid. Without exception, these chemical changes are the result of either acoustically produced cavitation or the progressive heating of the liquid through the absorption of the acoustical energy within the liquid. In Technical Report No. 17 an attempt was made to obtain information concerning the mechanism for sonochemical formation of hydrogen peroxide in oxygen saturated solutions by an isotopic tracer technique involving  $O^{18}$ . The experimental results indicated that in oxygen saturated solutions the O-O bond of the oxygen molecule is not formally broken during cavitation even at intensities of  $100 \text{ watts/cm}^2$ . In water saturated with oxygen at atmospheric pressure, approximately one-third of the peroxide oxygen is



TABLE I. Ultrasonic Absorption Apparatus Constructed and Used from 0.03 to 550 MHz.

Type of apparatus	Ultrasonic principle or modification	f (MHz)	Path (cm)	Volume (l.)
Resonator	radial mode reverberation in spherical resonator; computer controlled	0.02-0.3	--	12,50,100
Resonator	radial and axial mode in cylindrical resonator; computer controlled	.015-.03		.25
Reverberation	wide-band noise (statistical) reverberation	0.2-1	--	3
Carstensen HF send-receive	pulse technique; fixed transducer distance of 66 cm with variable solution/solvent path length to minimize diffraction effects; impedance match- ing; comparison method	0.7-14	66	29
VHF pulse echo	ultrasonic cell modification of apparatus to permit transducer-reflector alignment; pulse technique; variable path length; attenuator method; (attenuator matching devices)	5-65	20	0.035
VHP send-receive	modification of pulse echo to send-receive; pulse technique; send and receive transducers; ultra- sonic attenuation measured with a comparison signal generator; prototype for HF and UHF systems; impedance matching; diffraction loss correction	5-95	10	0.14
UHF send-receive	pulse technique; send-receive transducers on fused quartz delay lines; single tracking oscillator; impedance matching; comparison method	100-550	1	0.002

derived from oxygen gas and the remainder from the water. In 30% methanol-water solutions saturated with oxygen gas, all of the peroxide oxygen originates with the molecular oxygen and none from the water or methanol.

In contrast to sound wave induced chemical reactions in solutions, the degradation of polymers by ultrasonic waves can be explained by mechanical effects rather than thermal or chemical effects. In Technical Report No. 18 the rate of degradation of polystyrene in organic solvents by ultrasonic waves has been studied. It was concluded that degradation does not occur in the absence of cavitation even at acoustical intensities as high as 1000 watts/cm<sup>2</sup>. The extreme rates of shear in the liquid adjacent to a resonating cavitation bubble are believed to be responsible for the mechanical degradation of the polymers and represent an interesting means for studying the extreme mechanical effects associated with cavitation.

#### V. Advances in acoustic instrumentation

The most recent development in our laboratory has been the introduction of computers for controlling the acoustic measurements. A microcomputer controlled velocity and absorption measurements system was developed for cylindrical and spherical resonators. The microcomputer initiates predetermined frequency steps with the aid of a programmable synthesizer, with the output amplified and applied to the driving crystal. The received signal is fed into a programmable tuned amplifier and demodulated. When the computer finds a long decaying resonance mode, decay rate measurements were made and stored in a floppy disk for later analysis. The system allows for very detailed mode mapping of the resonator by accumulating frequency-amplitude data, along with a record of the temperature. The amplitude decay can be followed through 70 dB with reproducibility within  $\pm 0.2$  dB s<sup>-1</sup>. With this instrumentation a better defined relaxation

was obtained for 0.0041 M  $\text{MgSO}_4$  (Technical Report No. 48).

In order to obtain better results below 50 kHz, a 100 liter titanium sphere, on loan from Woodshole Oceanographic Institute, is interfaced to the computerized instruments. Q values as high as a million were observed around 20 kHz when the sphere was filled with distilled water.

The spherical resonators are not suitable for concentrated dispersions due to the fact that their narrow openings for introducing and removing material causes some difficulties in handling the dispersions. For this reason cylindrical resonators were built of polycarbonate. Using the lower radial modes of one of the resonators, a Q value of 1500 was obtained around 18 kHz, compared to  $Q = 900$  for similar resonators described in the literature. The better Q obtained in this work is probably due to the greater compliance of the polycarbonate material.

APPENDIX A

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APPENDIX B

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# Appendix C. Summary of ONR Sponsored Research in Physical Acoustics at CWRU

<u>Accomplishment</u>	<u>Significance</u>	<u>Coworkers</u>
1. The first detection and quantitative studies of ionic vibration potentials	Yields absolute partial molal volumes and important information concerning ion-solvent interaction in electrolytes.	R. Zana R. Dietrick
2. The first detection and quantitative measurements of polyelectrolyte vibration potentials; the development of a theoretical treatment of polyelectrolyte vibration potentials.	Information on counter ion binding and polyelectrolyte configuration in systems of both biological and industrial interest.	R. Zana J. Booker
3. The application of the ionic vibration potential technique to the study of micelles and the obtaining of evidence for the formation of clusters prior to micelle formation.	Results of interest from the standpoint of biological systems and detergent physical chemistry.	R. Zana
4. The quantitative study of colloidal vibration potentials.*	Quantitative verification of theory of charge distribution about colloidal particles in electrolytic solutions - of both biological and industrial interest.	J. Dereska J. Booker M. E. Gültepe Y. Chonde
5. Ultrasonic absorption measurements in colloidal dispersions in electrolytic solutions and identification of various loss mechanisms.†	Dispersed material in seawater contributes to sound absorption and scattering in long range sound transmission in the sea.	L. Jackopin F. Borsay M. E. Gültepe
6. Correction of erroneous data in the literature for ultrasonic relaxation in 2-2 electrolytes; development of a two-step rather than three-step model; quantitative studies of second order diffusion controlled processes in such electrolytes.	Understanding of fast chemical processes in electrolytic solutions; the principal process (MgSO <sub>4</sub> ) responsible for ultrasonic absorption in seawater below 10 <sup>5</sup> Hz.	L. Jackopin, L. Godlfarb, J. Stuehr

\* Research in progress during the past year.

Appendix C (continued).

7. Identification of various ultrasonic relaxation effects in other electrolytes including the tetraalkyl ammonium salts, and weak electrolyte and salts thereof, and the successful quantitative interpretation of these relaxations.
8. Quantitative results for the helix-random coil transformation in the model amino acid compound, poly-L-glutamic acid, and the finding that the transition is far less cooperative than had been expected.
9. Development of shock wave technique in a practical form for the study of relaxation processes in electrolytes at times as short as  $10^{-6}$  sec; use of this technique to obtain the first observation of relaxation in magnesium sulfate solutions, other than by ultrasonic techniques.
10. Identification of a relaxation in the borate-boric acid system in sea water with relaxation times of  $\sim 160 \mu$  sec using temperature-jump and shock wave techniques.
11. Brillouin and Rayleigh scattering measurements in electrolytic solutions; measurements of hypersonic velocities and absorption; measurements of intensity ratios of Rayleigh to Brillouin components.
12. Brillouin and Rayleigh (polarized and depolarized; scattering studies in hydrate melts (including supercooled) and molten salts; further evidence for visco-elastic relaxation in these systems.<sup>+</sup>

L. Jackopin,  
J. Broadhead

Understanding of the dynamics of electrolytic solutions; of interest to physical chemist and biologist.

J. Stuehr,  
A. Barksdale

Helpful information to molecular biologists in understanding the properties of amino acids.

H. Hoffmann

Method can be used to study relaxation at frequencies too low for practical ultrasonic laboratory measurements; has confirmed  $MgSO_4$  relaxation (the sea water problem).

R. Bressel,  
J. Micelli,  
P. Fisher

Provides the explanation for the low frequency relaxation encountered in acoustic propagation in sea water.

A. Maret

Extends ultrasonic measurements to gigahertz frequencies; confirmation of theory of concentration fluctuations in electrolytic solutions.

R. Carpio  
C. Petrovic  
F. Borsay  
B. Simic-Clavas

Information on liquid dynamics; helpful in understanding the super-cooling phenomenon.

<sup>+</sup> Research in progress during the past year.

Appendix C (continued)

- |   |   |   |
|---|---|---|
| 13. Low angle Brillouin scattering studies in electrolytes at frequencies down to low megahertz.  | Comparison of temporal and spatial relaxation; helpful in understanding phonon properties of liquids.   | F. Borsay   |
| 14. Ultrasonic absorption-velocity relaxation studies in hydrate melts (including supercooled). Identification of relaxation effects.*                                  | Helpful in understanding liquid dynamics and supercooling phenomena; interesting system for comparison of chemical relaxation and visco-elastic theory. | F. Borsay,<br>R. Bressel,<br>S. Smedley,<br>C. Hall |
| 15. The discovery of the acousto-electrokinetic effect.   | Has been used as probe for examination of acoustical fields.  | H. Dietrick,<br>F. Saunders                         |
| 16. Quantitative studies of the effects of sound waves (with and without cavitation) on mass transfer and boundary layers using schlieren techniques.                   | Demonstrated that ultrasonically produced cavitation greatly increases mass and heat transfer at solid-liquid boundaries.                               | R. Penn   |
| 17. Isotopic equilibration studies of cavitation, which have helped to define the temperature limits realized within cavitation bubbles during compression or collapse. | Provides explanation for chemical effects produced by intense sound waves.  | M. Del Duca   |
| 18. The establishment of the mechanism for the effects of intense sound waves on electrodeposition, corrosion and other electrode processes.                            | Potential application of intense sound waves to improve electroplating.   | R. Penn,<br>W. Wolfe                                |
| 19. Elucidation of the mechanism for ultrasonic degradation of polymers and also the initiation and promotion of polymerization.  | Provides bases for understanding damage to biological systems caused by intense sound waves.  | W. Roberts,<br>R. Fox                               |
| 20. Elucidation of mechanism for ultrasonic emulsification; role of surface waves.  | Considerable promise as method for producing emulsions.   | A. Patais   |
| 21. Interface electromodulation acoustic effect.*   | Information concerning the structure of water at electrode-electrolyte interface.   | F. Borsay<br>M. E. Gültape                          |

\* Research in progress during the past year.

Appendix C (concluded)

22. The first detection and qualitative study of the effect of hetero-deflocculation of two dissimilar mineral grains on the velocity of sound in concentrated dispersions of kaoline-montmorillonite mixtures.<sup>+</sup>

Provides information for better understanding of sound propagation in sediments and the multi-component colloidal dispersions.

M.E. Gültepe  
M.A. Barrett-  
Gültepe

23. A micro-computer controlled velocity and absorption measurements with cylindrical and spherical resonators and using this system with a 100 L titanium spherical resonator.<sup>+</sup>

The computer controlled experiments gives better defined relaxation curves with greater accuracy and reproducibility.

M.E. Gültepe  
M.A. Barrett-  
Gültepe

24. The first detection and qualitative study of the effect of adsorbed species and configurational changes of this adsorbed layer on the velocity of sound in the concentrated dispersions of a model colloid.<sup>+</sup>

Understanding of the structure of the adsorbed macromolecules at electrochemical interfaces.

M.E. Gültepe  
M.A. Barrett-  
Gültepe

25. Development of computerized resonator system for absorption measurements in electrolytes and colloidal systems

Very substantially extends the capability of the resonator method.

M.E. Gultepe  
M.A. Barrett-  
Gultepe

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<sup>+</sup>Research in progress during the past year.

February 1981

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